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MICROMEDIA

KINETIC STUDIES OF COKE FORMATION IN HYDROCARBON FRACTIONS OF HEAVY CRUDES

by

Dwijen K. Banerjee*, Keith J. Laidler*,
Biswanath N. Nandi**, and David J. Patmore**

ABSTRACT

Different types of bitumens [Athabasca bitumen, topped Athabasca bitumen, Cold Lake heavy oil, and light Arabian vacuum bottoms (pitch)] were separated into five fractions classified as follows: asphaltene, soft resin, hard resin, aromatics and saturates. The various fractions, and the bitumens themselves, were then kept at temperatures ranging from 395°C to 510°C, and measurements made of the amounts of coke produced as a function of time. The results were analyzed to give rate constants and activation energies for coke (toluene insoluble) formation. It was found that the rate of coke formation is greater the higher the degree of aromaticity of the feed stock. The results have led to a tentative mechanism for the formation of coke, which appears to be formed by a rapid reaction from large aromatics formed as intermediates.

(Keywords: bitumen; coke formation; asphaltenes; resins)

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INTRODUCTION

When bitumen is processed at elevated temperatures there is usually a tendency for coke formation, and this could lead to some technical difficulties. It is therefore important to gain some understanding of the mechanism of coke formation from bitumen and other heavy crudes. The matter is complicated, since heavy crudes are mixtures of many components, the proportions of which vary considerably according to the source of the material. It is, however, possible to separate a heavy crude into fractions, and in the present investigation a separation has been made into five fractions: asphaltene, soft resin, hard resin, aromatics and saturates. Kinetic measurements were made of coke formation from heavy crude obtained from different sources, and also of coke formation from the five fractions obtained from each of the four heavy crude samples.

Kinetic studies have as a main objective the formulation of a mechanism for the process investigated and the present results have led to a tentative mechanism that can be modified and refined by further studies. An understanding of the mechanism of coke formation will certainly also help in the problem of reducing the extent to which the process occurs under practical conditions.

There have been no previous systematic studies of the kinetics of coke formation from different heavy crude fractions. Some previous studies, however, have provided useful information about the process.

George et al.[1] studied coke formation from the pyrolysis of Athabasca Oil sand bitumen in the presence of calcium hydroxide, and Babu and Cormack[2] studied the effect of low temperature oxidation on the coke residue from Athabasca bitumen. Speight[3] investigated the thermal cracking of Athabasca bitumen, Athabasca asphaltene, and deasphaltened heavy oil; he concluded that the repeated condensation of aromatic material leads to coke formation. Nandi et al.[4] reported two different types of coke residue, one obtained from heavy oil aromatic fractions and the other from asphaltened from Athabasca bitumen. Shu and Venkatesan[5] investigated the kinetics of thermal visbreaking of Cold Lake bitumen. They measured the changes in viscosity during the thermal visbreaking of the bitumen as a function of time and temperature, and using a first-order kinetic model they calculated the Arrhenius

activation energy. Henderson et al.[6] calculated the rate constant of visbreaking of Athabasca bitumen. Sekhar and Ternan[7] reported that the pyrolysis of pitch follows first-order kinetics, and that the apparent activation energy and pre-exponential factor both increased as reaction proceeded.

EXPERIMENTAL

Materials Used

The following four heavy crudes were used in the investigation:

(1) Athabasca bitumen
(2) Topped Athabasca bitumen
(3) Light Arabian vacuum bottoms (pitch)
(4) Cold Lake heavy oil

The following materials were used for the separation of the bitumens:

(a) Silica gel, grade 923, 100-200 mesh, W.R. Grace and Co. DCD, Baltimore, MD.
(b) Activated alumina, grade AX-0612-3, type F-20, 80-200 mesh, MCB Manufacturing Chemists, Cincinnati, Ohio.
(c) Attapulgus clay, grade AX-1799, 30-60 mesh, MCB Manufacturing Chemists, Norwood, Ohio.
(d) Solvents - HPLC grade obtained from Fisher Scientific, Ottawa, Ontario.

Procedure

All of the heavy crudes were separated into five fractions. Deasphalting was carried out by the following method[8]. A 5 g sample of heavy crude was dissolved in 5 mL of benzene, and 40 times the volume (200 mL) of n-pentane was added with thorough shaking. The mixture was then kept in the dark for 10 h with occasional shaking. The contents were filtered and the precipitate washed with n-pentane until a clear solution was obtained. The n-pentane extract, maltene, was kept for later treatment; the precipitate was dried and weighed as asphaltene.

Further separation of maltene was carried out by adsorption column chromatography using the Syncrude analytical method[9] which is also recommended by ASTM-D2007-80. Maltene was first separated into resins and oil on an attapulgus clay column. The clay was activated at 150°C for 3 h prior to use.

The n-pentane extract, after removal of asphaltene, was concentrated to about 20 mL, and applied to the clay column; the oil was then eluted from the column with 200 mL n-pentane.

The column was then dried by passing nitrogen through it and the soft resin then eluted with 100 mL of methyl ethyl ketone. The column was then dried and the hard resin eluted with 100 mL tetrahydrofuran. Both extracts were dried under vacuum, then at 100°C for 10 min. The soft resin was obtained as a dark highly viscous oily liquid, and the hard resin as a dark semi-solid.

The n-pentane extract of oil eluted from the clay was further separated into aromatics and saturated hydrocarbons, in a chromatographic column packed with activated alumina and silica gel. Both were activated at 150°C for 3 h prior to use.

The n-pentane extract of oil was concentrated to about 5 mL, and was injected into the alumina. The column was then treated with 150 mL n-pentane to elute the nonaromatics, and the aromatic fraction was then eluted with 75 mL toluene. The solvents were removed under vacuum, and the residues were weighed.

Analysis

The elemental analyses for carbon, hydrogen, nitrogen, sulphur and oxygen were carried out for all of the fractions. The fractions were also characterized by ^{1}H NMR and IR analyses.

Kinetic measurements

For the pyrolysis experiments a special temperature-programmed furnace, supplied by Lindberg, Wisconsin, was used. The furnace was modified in the laboratory to allow a quartz boat to be hung inside the furnace, and to allow dry nitrogen to pass through the system. The furnace could be programmed for a given range of temperatures at a given rate of heating. The temperature could be maintained constant at a specified temperature for a certain time, and could then be rapidly cooled.

The bitumen and its fractions were pyrolyzed within the temperature range of 390-510°C at various contact times from 3 to 15 min, in an inert atmosphere of oxygen-free dry nitrogen. About 200 mg of each sample was placed in a quartz boat which was inserted into the furnace preheated to the required temperature.

The sample was kept at a predetermined temperature for a known time, then it was taken out of the furnace. It was cooled rapidly by blowing nitrogen through it to avoid further reactions. The residue formed in the boat was then extracted with toluene and filtered; the toluene insoluble was defined as coke. The residue formed was dried at 120°C in an oven; the yield of coke was determined, and the coke was then ashed over a Bunsen burner.

RESULTS

Fraction Analyses

The relative percentages of the five major fractions are listed in Table 1 for the four heavy crudes. The results of the elemental analyses on each of the fractions are given in Table 2. Some characterization of the functional groups of the various fractions was also made by ^{1}H NMR and IR analyses which will be published in a separate paper.

Kinetic Results

Figures 1 to 4 show the amounts of coke produced as a function of time and also show, as a function of temperature, the amount produced in a period of 5 min. The amounts of coke are expressed as percentages of ash-free crude oil. Each of the four figures is for a different crude oil, and each shows results for different fractions.

In all cases the rates of coke formation are greatest for the asphaltenes, followed by the resins. For the light Arabian vacuum bottoms and Cold Lake heavy oil, the hard resin produced coke somewhat more rapidly than the soft resin. However, the soft resin from Athabasca bitumen produced coke more rapidly than hard resin. For the resins from the topped Athabasca bitumen, the order is reversed at 440°C; below that temperature the soft resin produced coke more rapidly, while above 440°C the coke formation was more rapid with the hard resin. The differences between the hard and soft resins, however, are always small.

The aromatic fractions in all cases produced coke considerably less rapidly than the asphaltenes. In fact, up to 440°C only insignificant amounts of coke were obtained from the aromatics over the period of the experiments (5 min). All of the kinetic measurements had to be made above that temperature. Very little coke formation was found with the saturates, and no kinetic

measurements were made; the rates of coke formation were always less than one-tenth of the rates with the aromatic fractions.

The first-order rate constants obtained from the results are listed in Table 3; it had previously been demonstrated by McNab et al.[10] that coke formation follows first-order kinetics.

Figures 5 to 8 show Arrhenius plots, of ln k against 1/T, where T is the absolute temperature. The plots are linear within the experimental error, and from the slopes the activation energies were calculated; these are listed in Table 4.

DISCUSSION AND CONCLUSIONS

Analytical Results

The results listed in Table 1 show that the amounts of asphaltene were significantly smaller for Athabasca bitumen and light Arabian vacuum bottoms compared with topped Athabasca bitumen and Cold Lake heavy oil. The distillation of Athabasca bitumen increases its asphaltene and resin contents; these high boiling components remain in the residue after distillation.

The total resin content is highest in Cold Lake heavy oil, partly because of the higher amount of hard resin. The soft resin is always present in much larger amounts than the hard resin. Athabasca bitumen has a much higher proportion of aromatics than the others, followed by light Arabian vacuum bottoms.

The H/C ratios listed in Table 2 provide an inverse meausure of the degree of aromaticity. The results show that the asphaltenes always have the highest aromaticities. They also have the maximum amounts of sulphur and nitrogen.

The resins are the next most aromatic fractions, and they contain the largest proportions of oxygen. There are slight differences between the aromaticities of the resins from various sources, as well as between the hard and soft resins.

Kinetic Results

The results shown in Figs. 1 to 5 and summarized in Table 3 show that the order of the rate constants is as follows:

asphaltene > resins > aromatics > saturates

This is also the order of decreasing aromaticities, as revealed by the H/C ratios (Table 2). This supports the view that aromaticity plays an important role in determining the rate of coke formation. The processes of coke formation from the aromatics have slightly higher activation energies (52 to 58 kJ mol^{-1}) than the corresponding processes from the resins (34 to 40 kJ mol^{-1}) and the asphaltenes (41 to 47 kJ mol^{-1}). This means that the rates of coke formation vary with temperature more strongly for the aromatics than for the other fractions.

Other factors besides aromaticity also seem to be signficant. Asphaltene is a high molecular weight substance having a very condensed structure[11], whereas the resins are reported to have less condensed structures[12]. this difference in structure may therefore contribute to the kinetic results. This is supported by the result that the rates of coke formation are usually greater for the more condensed hard resins than for the less condensed soft ones.

The dominant influence of aromaticity can also explain the kinetic variations between fractions obtained from different types of bitumen. For example, the asphaltenes and resins from topped Athabasca bitumen are more aromatic than those from the original Athabasca bitumen (Table 2), and they have higher rates of coke formation (Table 3). Support for the conclusion that aromaticity is of paramount importance is provided by recent results of Dickakian[13] in coke production from pitch carbonization; he found that the coke is formed mainly from the highly polycondensed aromatic heptane-asphaltene fraction.

To explain the results the reaction scheme in Fig. 9 is tentatively suggested. In this scheme the coke is formed in a fast reaction from large aromatic molecules (reaction 10), which in turn are produced by the condensation of small aromatic molecules (reaction 7) or through the formation of resins (reaction 8) or of asphaltene (6 and 9). The formation of large aromatics and hence coke is postulated to be more rapid from asphaltene (reaction 9) than from resins and the small aromatics; this is consistent with the observed relative rates.

The saturated hydrocarbons form coke very slowly, and this is attributed to the fact that their formation of large aromatics involves a number of steps, shown in Fig. 9.

The results and interpretation we have proposed provide an explanation for the rates of coke formation from the heavy crude themselves. The order is:

Topped Athabasca bitumen > Cold Lake heavy oil > Athabasca bitumen > and Arabian vacuum bottom.

As seen from Table 1, this is also the order of the amounts of asphaltene and resins present.

ACKNOWLEDGEMENTS

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Table 1 - Analyses of heavy crudes

	Athabasca bitumen	Topped Athabasca bitumen	Cold Lake heavy oil	Light Arabian vacuum bottom (pitch)
Asphaltene	18.2	30.4	24.9	17.2
Soft resin	19.2	25.6	27.1	24.6
Hard resin	4.3	3.6	10.3	3.3
Aromatics	36.5	27.6	20.7	31.0
Saturates	21.8	12.8	17.0	23.9

Table 2 - Results of elemental analyses of the fractions of heavy bitumen

	C	H	N	O	S	H/C	N/C	O/C	S/C
Athabasca bitumen									
Asphaltene	79.7	7.9	1.2	1.8	7.9	1.18	0.0128	0.017	0.037
Soft resin	79.8	9.7	0.9	3.6	4.7	1.46	0.008	0.034	0.022
Hard resin	78.6	9.8	0.7	4.7	4.8	1.49	0.0105	0.045	0.023
Aromatics	89.5	10.9	-	-	-	1.46	-	-	-
Saturates	80.5	11.6	-	-	-	1.73	-	-	-
Topped Athabasca bitumen									
Asphaltene	79.2	7.5	1.3	1.6	6.6	1.13	0.014	0.015	0.031
Soft resin	81.1	9.2	0.9	2.1	5.3	1.34	0.010	0.019	0.024
Hard resin	83.9	9.7	0.5	2.9	2.2	1.38	0.005	0.026	0.009
Aromatics	83.3	10.1	-	-	-	1.45	-	-	-
Saturates	86.4	12.8	-	-	-	1.78	-	-	-
Cold Lake heavy oil									
Asphaltene	81.4	8.0	1.2	1.3	6.3	1.18	0.013	0.012	0.029
Soft resin	75.1	9.3	0.6	9.9	4.1	1.49	0.007	0.098	0.020
Hard resin	68.6	8.3	0.7	9.6	5.2	1.45	0.009	0.105	0.028
Aromatics	86.8	10.2	-	-	-	1.41	-	-	-
Saturates	86.4	13.3	-	-	-	1.84	-	-	-
Light Arabian vaccum bottoms (pitch)									
Asphaltene	84.6	7.4	1.0	0.6	6.4	1.04	0.010	0.005	0.028
Soft resin	83.4	9.5	0.7	1.4	5.1	1.36	0.007	0.012	0.023
Hard resin	81.8	9.4	0.6	3.7	3.4	1.38	0.006	0.034	0.016
Aromatics	86.5	10.7	-	-	-	1.48	-	-	-
Saturates	86.4	13.5	-	-	-	1.87	-	-	-

Table 3 - Rate Constants for coke formation

		Rate constant/min^{-1}			
	Temp °C	Asphaltene	Soft resin	Hard resin	Aromatics
Athabasca bitumen					
	395	-	0.12	-	
	400	0.17	-	0.13	
	420	0.23	0.14	0.15	
	440	0.26	0.17	-	
	450	-	-	0.19	
	460	0.37	0.19	-	
	465			-	0.08
	470			0.22	-
	480				0.10
	495				0.13
	510				0.15
Topped Athabasca bitumen					
	400	0.19	0.18	0.17	
	420	0.26	0.22	0.20	
	440	0.33	0.27	0.24	0.07
	460	0.38	0.31	0.32	0.10
	470				0.13
	490				0.15
Cold Lake heavy oil					
	400	0.21	0.16	0.15	-
	420	-	0.21	0.18	-
	430	0.25	-	-	-
	450	0.29	0.26	0.25	0.06
	470	0.40	0.34	0.31	0.08
	490	-	-	-	0.10
	510	-	-	-	0.12
Light Arabian vacuum bottoms (pitch)					
	400	0.22	0.18	0.17	
	420	0.27	0.21	0.20	
	440	0.38	0.25	0.25	
	460	0.43	0.33	0.33	
	470				0.08
	490				0.11
	510				0.15

Table 4 - Energies of activation for coke formation from heavy crude fractions

	Activation energy/kJ mol^{-1}			
Fraction	Athabasca bitumen	Topped Athabasca bitumen	Cold Lake heavy oil	Light Arabian vacuum bottom (pitch)
Asphaltene	44	47	41	46
Soft resin	37	36	40	39
Hard resin	35	34	40	40
Aromatics	57	58	52	55

Figure Captions

Fig.1 - Results for Athabasca bitumen. •- asphaltenes, o- soft resin, x- hard resin, Δ- aromatics, ▲ - bitumen.
   a. Coke formation as a function of time at 400°C, except for aromatics at 465°C.
   b. Coke formation as a function of temperature at a residence time of 5 min.

Fig.2 - Results for topped Athabasca bitumen. Symbols same as Fig.1.
   a. Coke formation as a function of time at 400°C, except for aromatics at 475°C.
   b. Coke formation as a function of temperature at a residence time of 5 min.

Fig.3 - Results for Cold Lake heavy oil. Symbols same as Fig.1.
   a. Coke formation as a function of time at 400°C, except for aromatics at 470°C.
   b. Coke formation as a function of temperature at a residence time of 5 min.

Fig.4 - Results for light Arabian vacuum bottoms(pitch). Symbols same as Fi
   a. Coke formation as a function of time at 400°C, except for aromatics at 470°C.
   b. Coke formation as a function of temperature at a residence time of 5 min.

Fig.5 - Arrhenius plots for the fractions from Athabasca bitumen.

Fig.6 - Arrhenius plots for the fractions from topped Athabasca bitumen.

Fig.7 - Arrhenius plots for the fractions from Cold Lake heavy oil.

Fig.8 - Arrhenius plots for the fractions from light Arabian vacuum bottoms (pitch).

Fig.9 - Tentative reaction scheme for coke formation.

FIGURE CAPTIONS

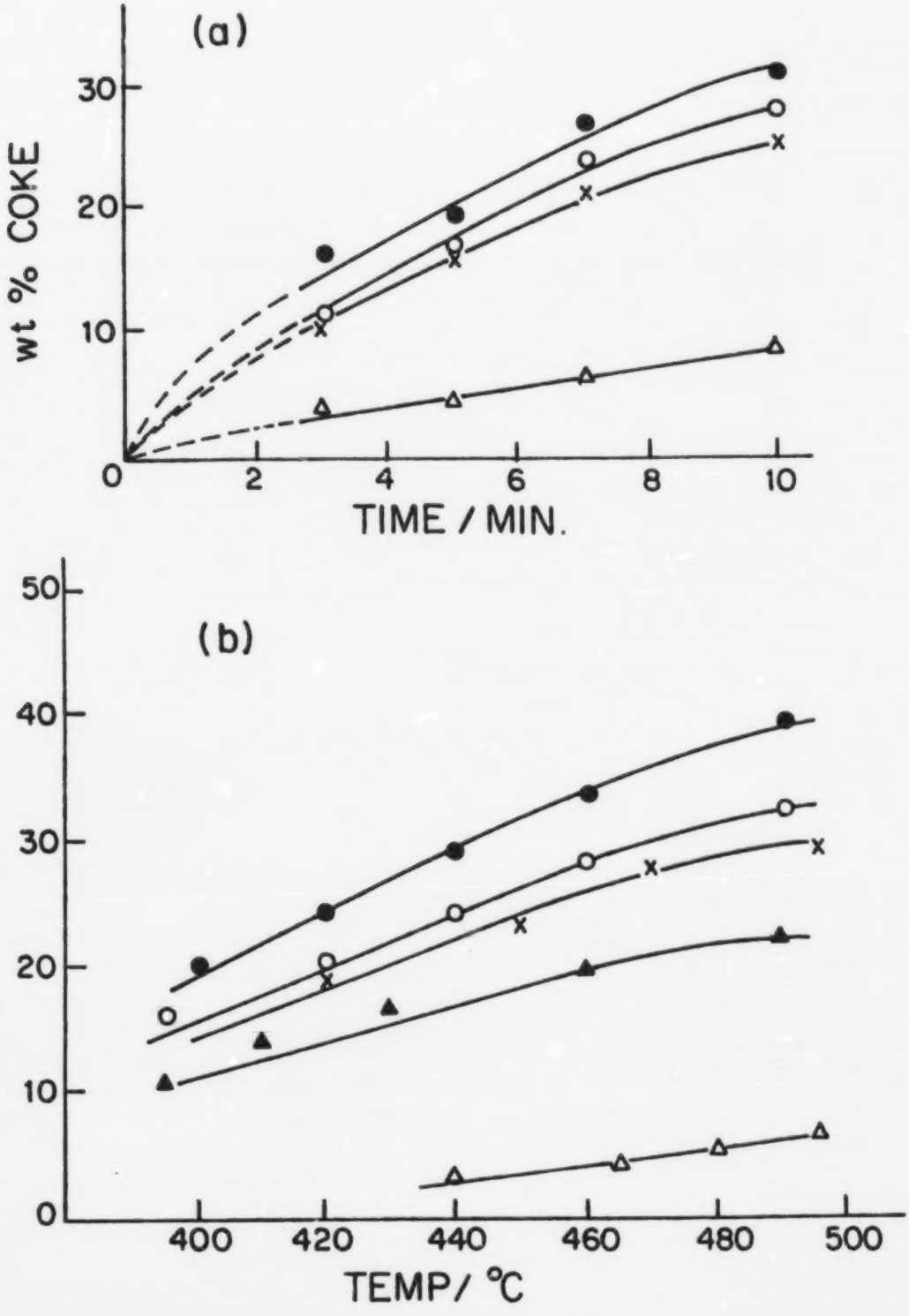
Fig. 5 - Arrhenius plots for the fractions from Athabasca bitumen.

Fig. 6 - Arrhenius plots for the fractions from topped Athabasca bitumen.

Fig. 7 - Arrhenius plots for the fractions from Cold Lake heavy oil.

Fig. 8 - Arrhenius plots for the fractions from light Arabian vacuum bottoms (pitch).

Fig. 9 - Tentative reaction scheme for coke formation.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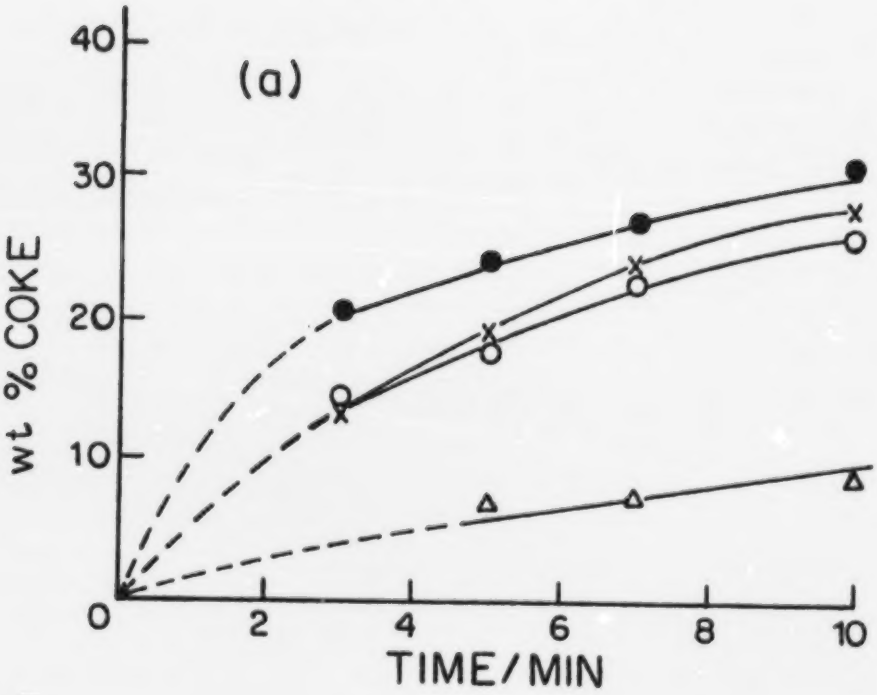
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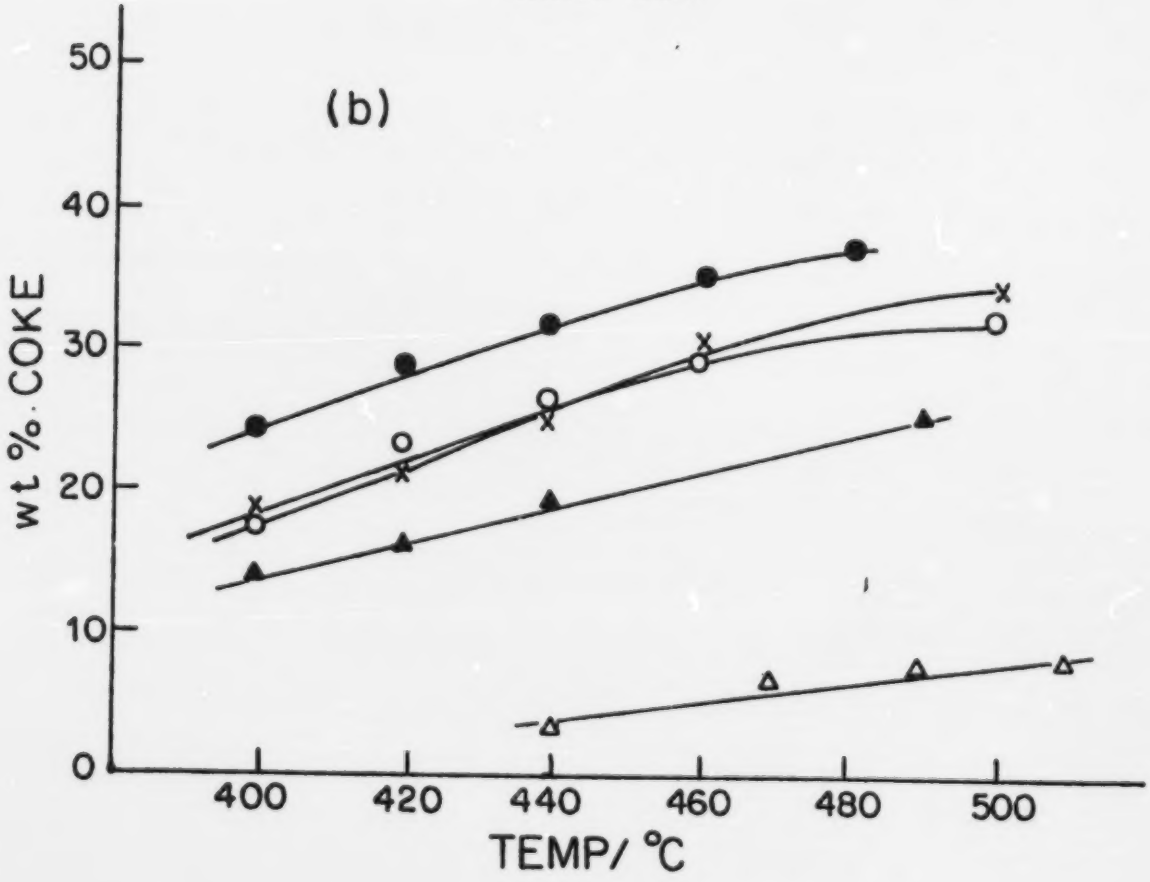
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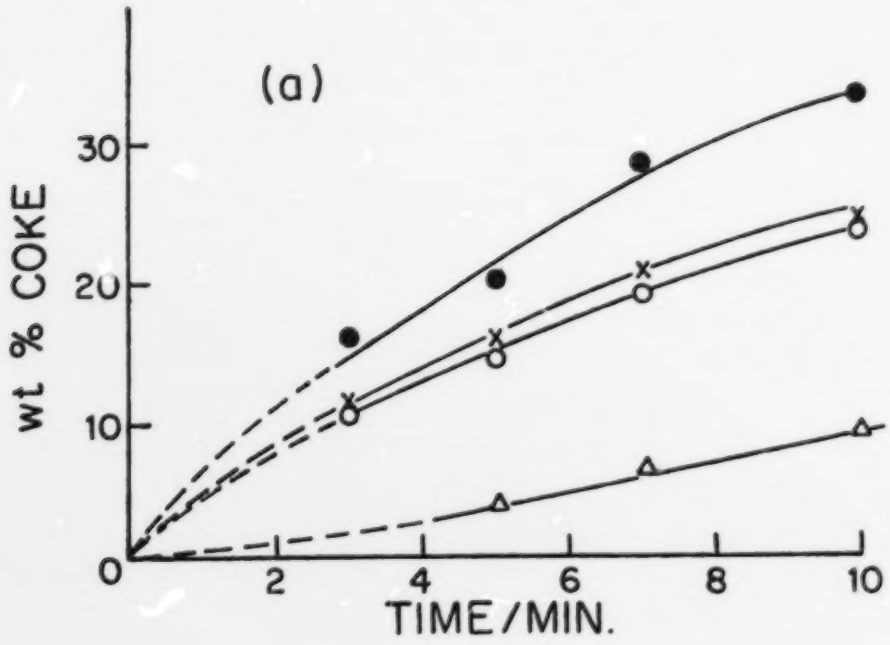
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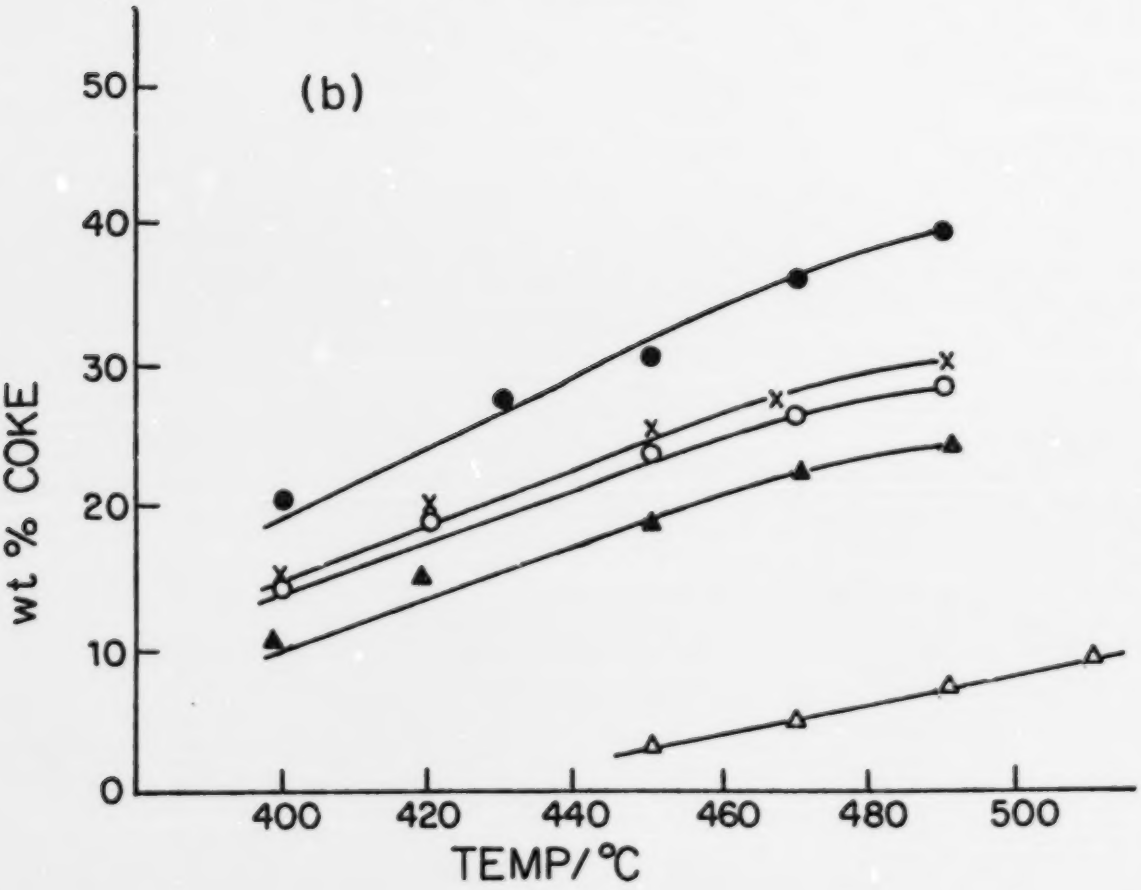
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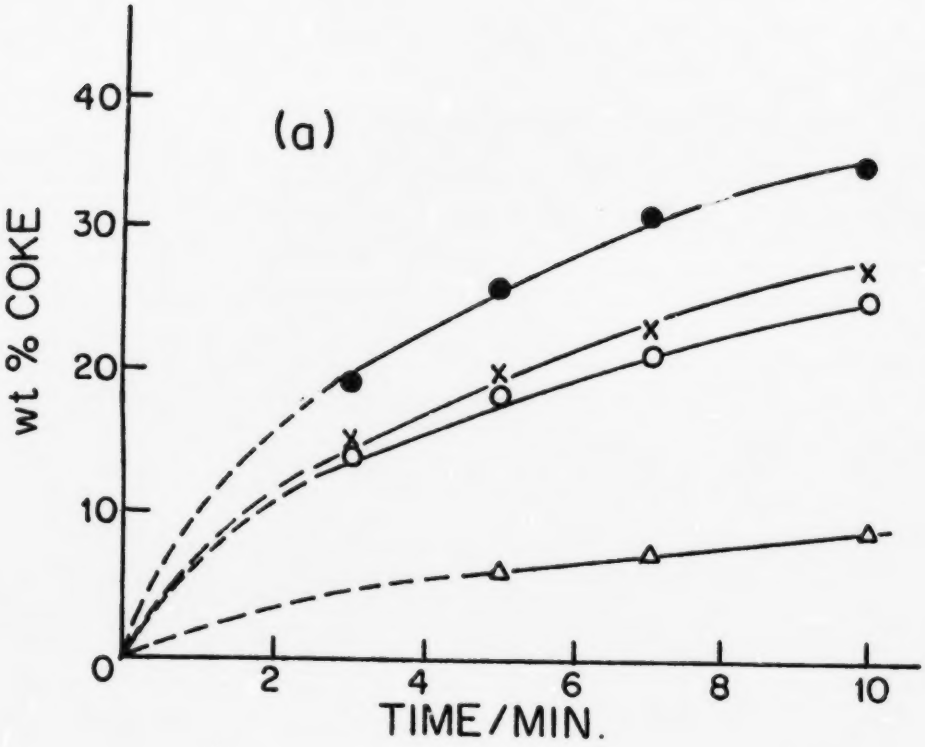
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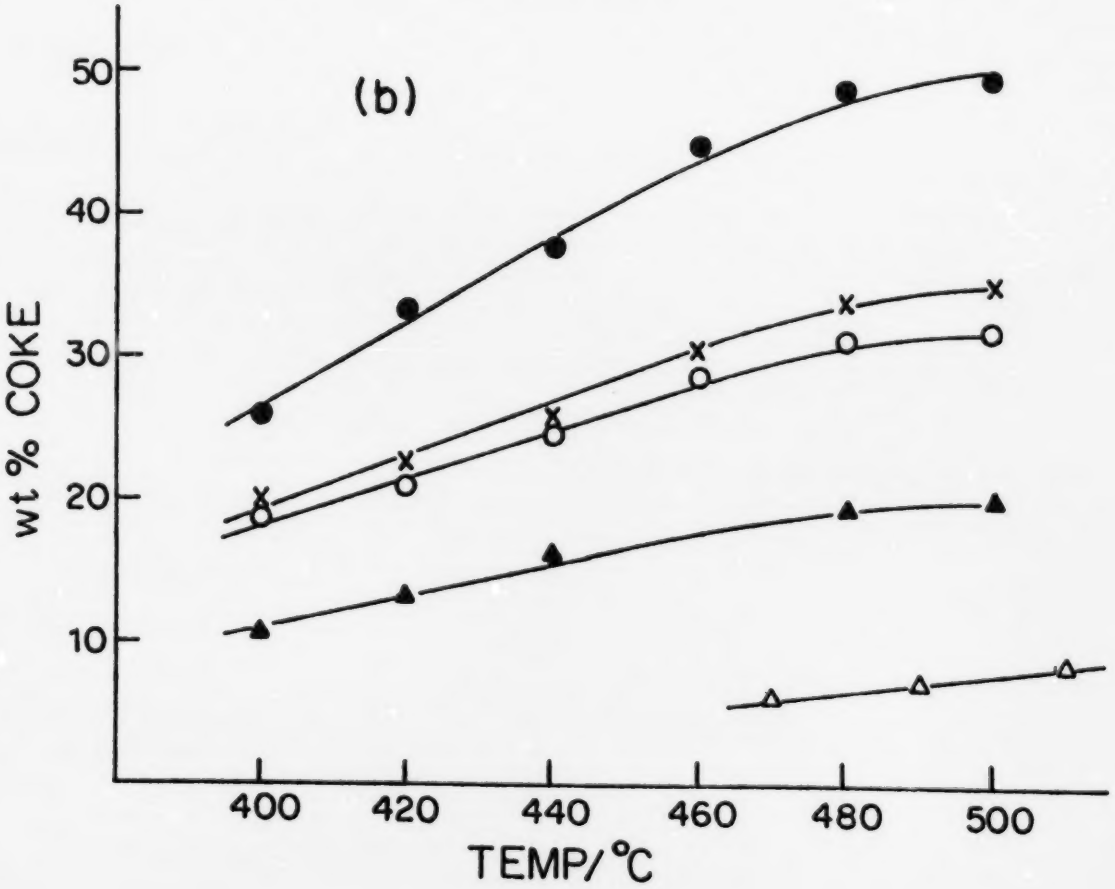
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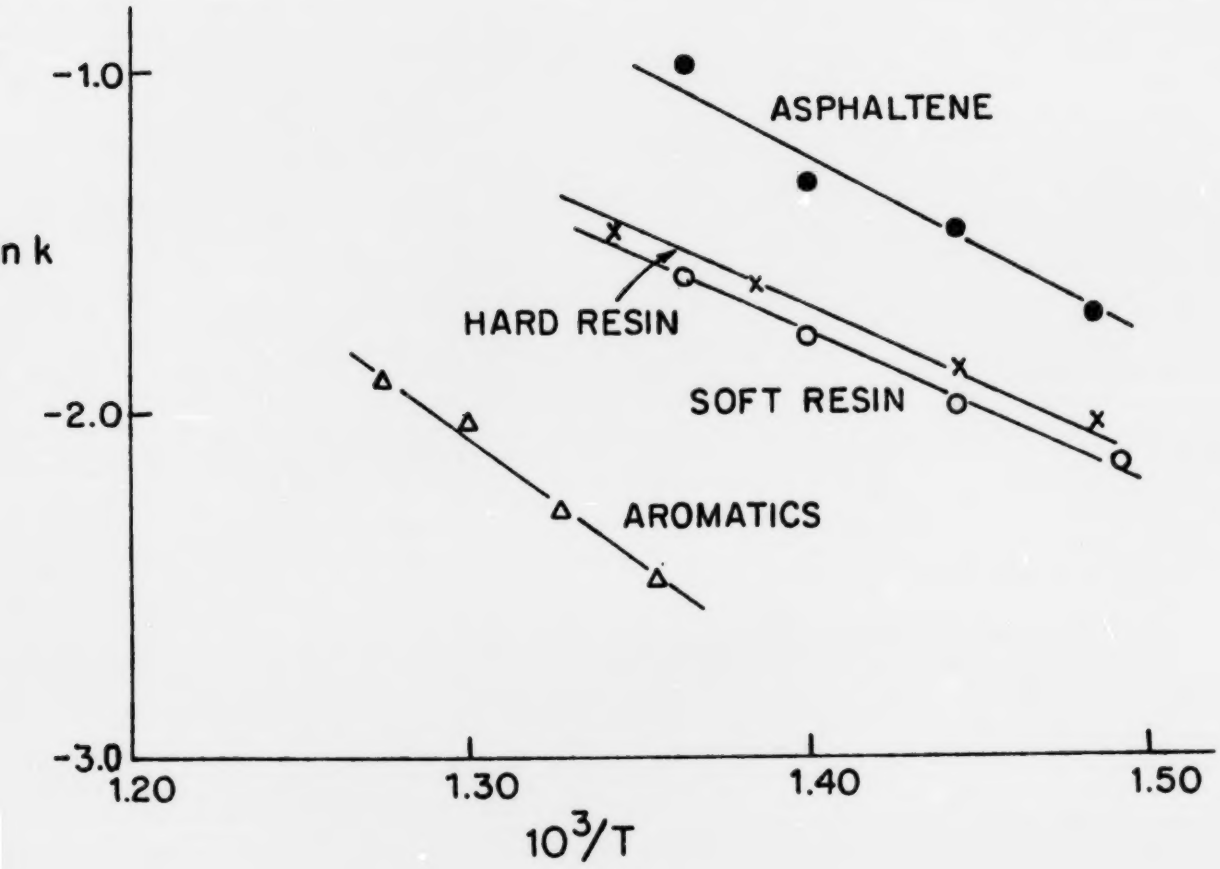
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SOFT RESIN
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10³/T

Fig 5

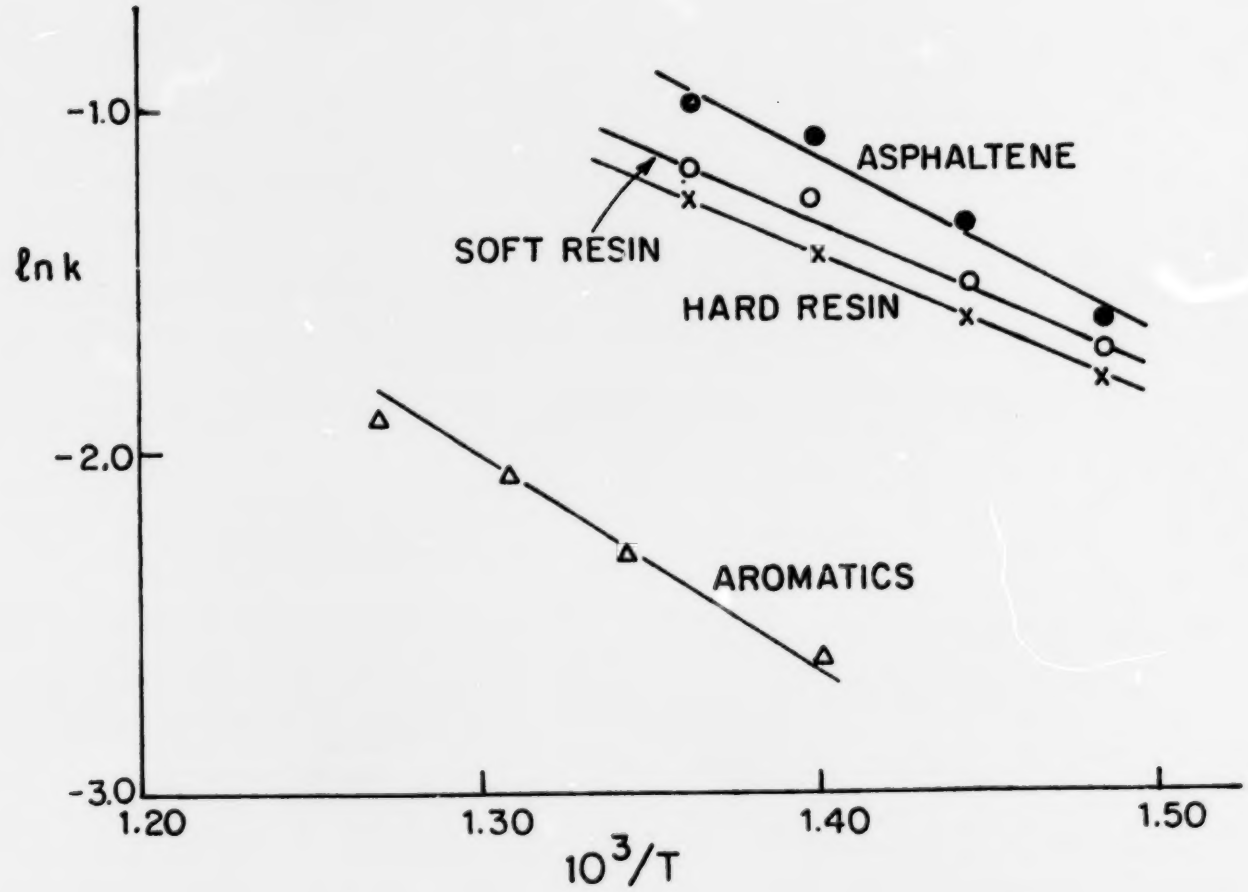
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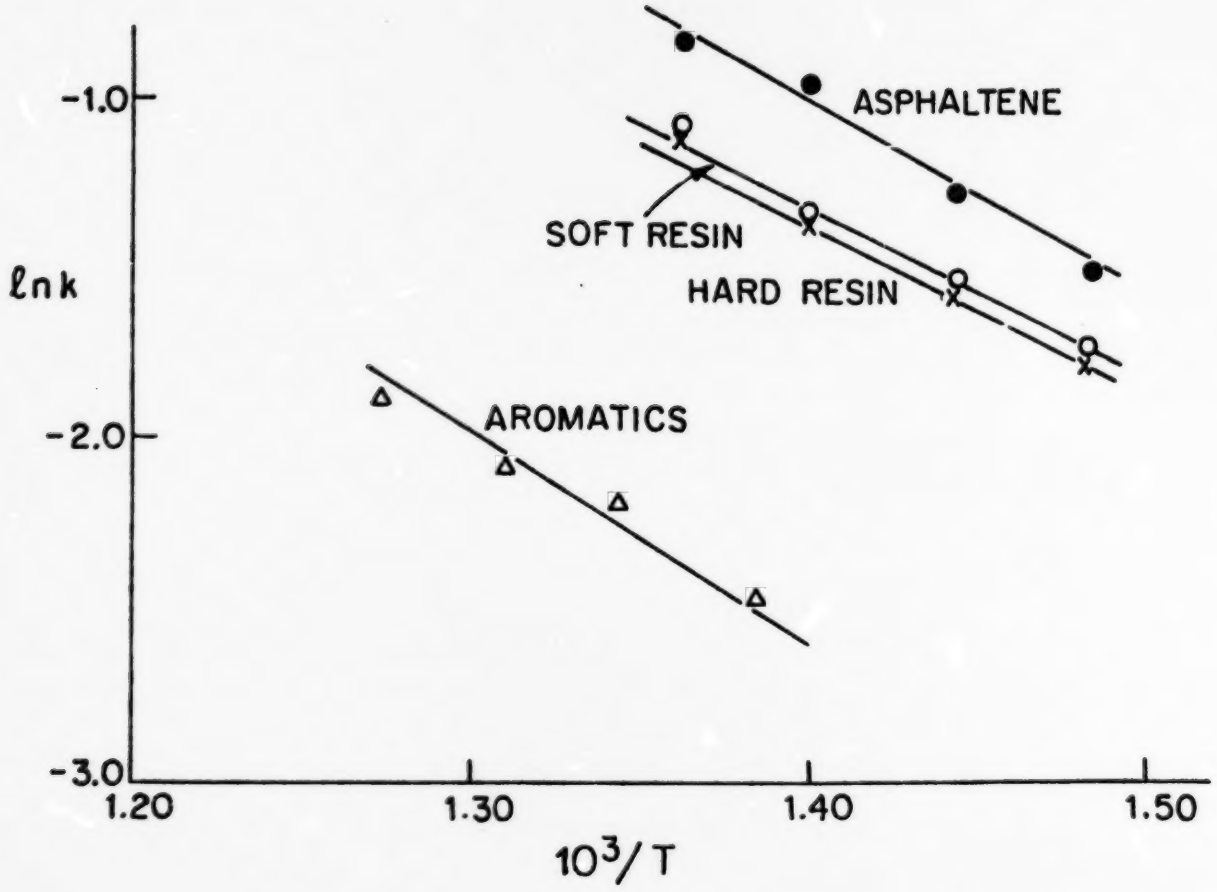
Fig 6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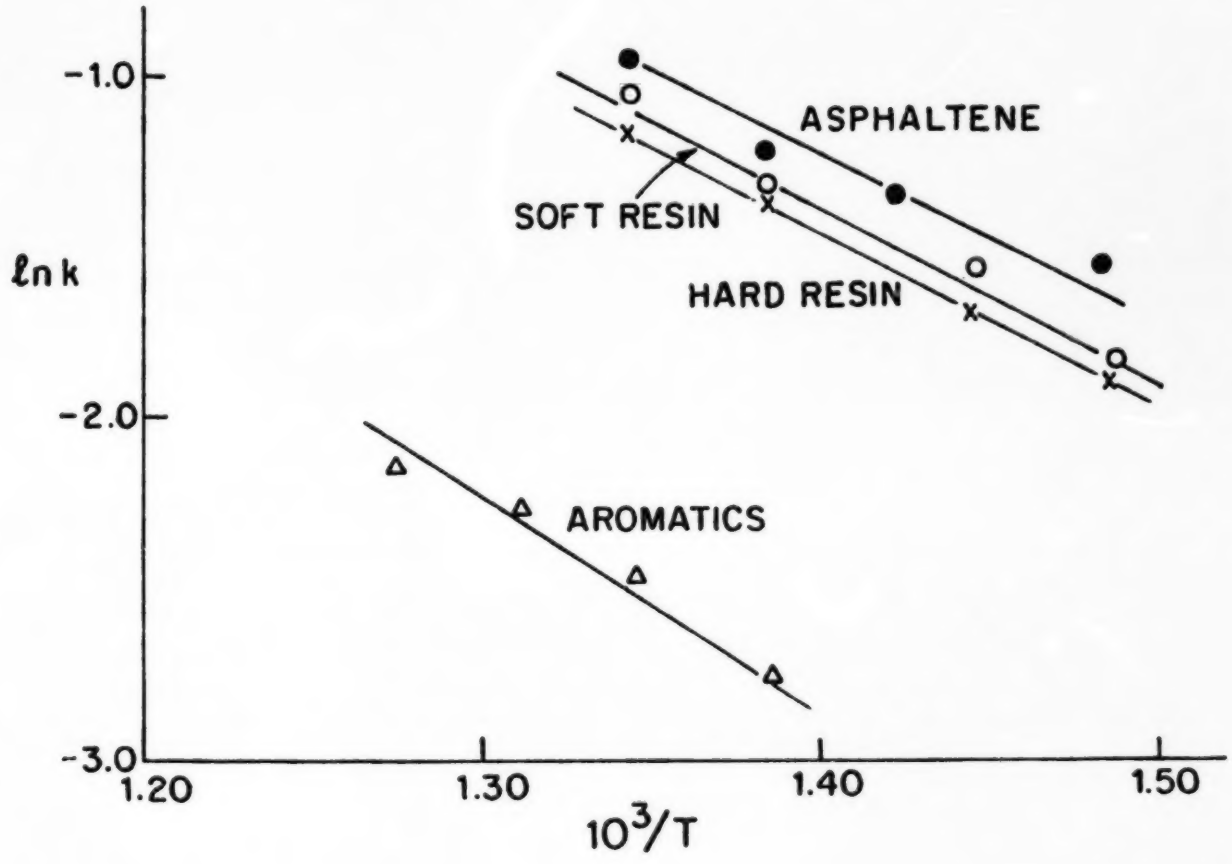
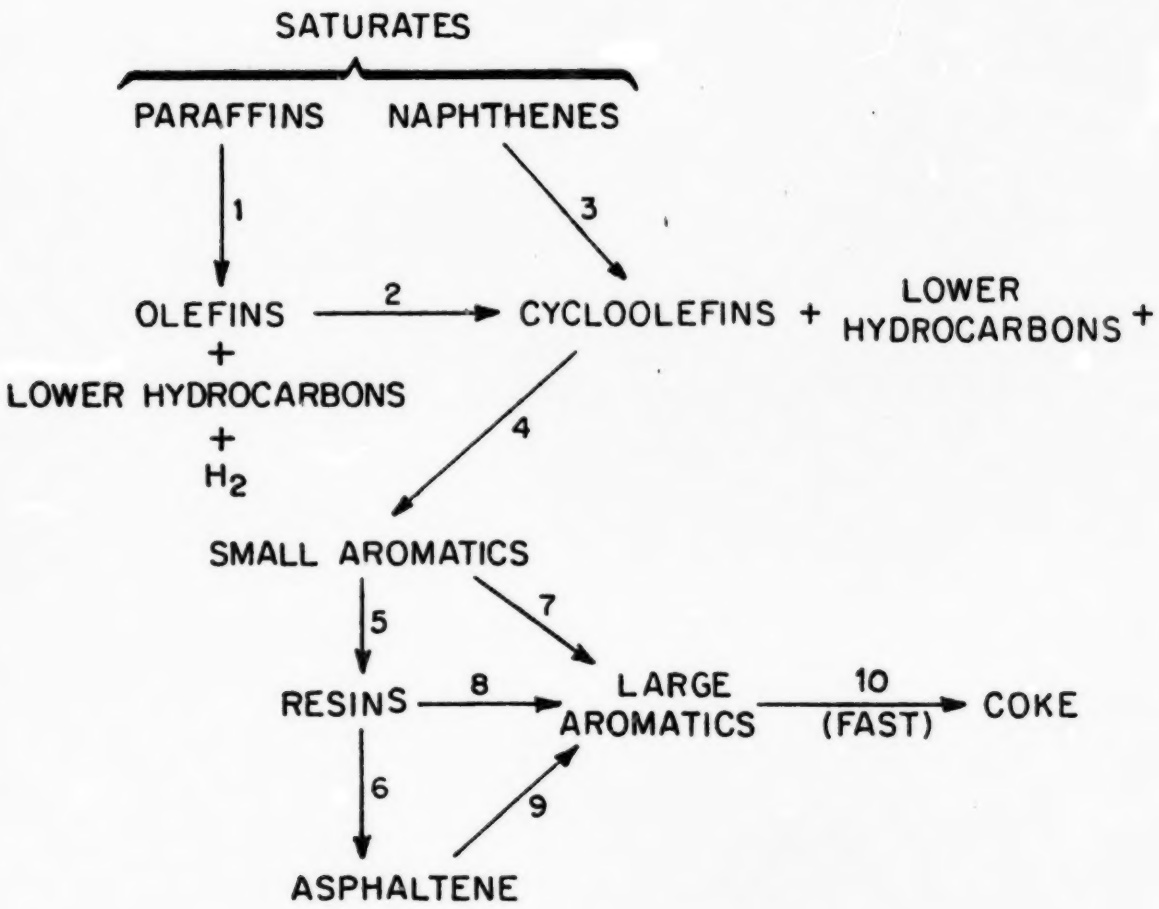
1.50
10³/ T


-1.0
-2.0
-3.0
ln k
ASPHALTENE
SOFT RESIN
HARD RESIN
AROMATICS
1.20
1.30
1.40
1.50
10³/T


SATURATES
PARAFFINS
NAPHTHENES
1
3
OLEFINS
2
CYCLOOLEFINS
+
LOWER HYDROCARBONS
+
LOWER HYDROCARBONS
+
H_2
4
SMALL AROMATICS
5
7
RESINS
8
LARGE AROMATICS
10
(FAST)
COKE
6
9
ASPHALTENE

POOR
QUALITY
ORIGINAL